

Thermosensitive Hydrogels Based on IPNs and Emulsion Blends of Poly (N-isopropylacrylamide) and Polyurethane

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Introduction

Thermally reversible hydrogels undergo dramatic volume change to temperature change and a number of applications as coating materials as well as biomedical and agricultural industry [1]. Among them poly (N-isopropylacrylamide) (PNIPAAm) shows a lower critical solution temperature (LCST) at 32°C and its thermosensitivity has extensively been investigated in drug delivery system [2].

For specific application, mechanical properties of the gels, that is the mechanical properties at swollen state is generally poor and reinforcement is often desired. Following our earlier work [3] compression strength of polyacrylamide gel has been increased over 100% when 10% of polyurethane (PU) was incorporated as IPNs.

In this paper, we prepared IPN-based and emulsion blend of PNIPAAm with PU hydrogels in order to overcome the shortcomings of a normal PNIPAAm hydrogels. These hydrogels have been tested for mechanical properties by universal testing machine. The temperature dependences of the swelling ratio of these PU-PNIPAAm hydrogels were also characterized to determine their thermo-response capability.

Experimental

Materials. Extra pure grades of 4,4'-dicyclohexylmethane diisocyanate(H₁₂MDI), poly(tetramethylene glycol) (PTMG; $\bar{M}_n=650$), dimethylol butanoic acid (DMBA), dibutyltin dilaurate (DBTDL), 1,4-butane diol(1,4-BD), and 2-hydroxy ethylacrylate (HEA) were used to prepare VTPU. PNIPAAm was mixed with N-isopropylacrylamide (NIPAAm), N,N'-methylenebisacrylamide (MBAAm), and potassium persulfate(KPS) before it was subject to reaction.

Synthesis. H₁₂MDI, PTMG, DMBA, 1,4-BD, and DBTDL were first mixed and reacted at 80°C to obtain NCO-terminated prepolymer. Then HEA was added and reacted for 4hrs to obtain vinyl terminated prepolymer (VTP). Dispersion of PU prepolymer was carried out by adding distilled water into VTP. After radical polymerization of VTP, NIPAAm monomer, MBAAm, and KPS were added to the dispersion of PU. Then polymerization/cross-linking of the NIPAAm monomer and cross-linker MBAAm were carried out at 25°C for 24h. Thereafter, an IPNs structure, consisting of PU network and PNIPAAm network components, was formed. Emulsion blends were obtained by blending networked PU dispersion and PNIPAAm emulsion throughout emulsion polymerization.

Characterizations. Number average diameter of dispersion was measured by light scattering method (Autosizer, Malvern IIC).

To measure the equilibrium swelling ratio, samples were immersed in water at 20, 30, 35, 40, 50, and 60°C for fixed period of time. Equilibrium swelling ratio was defined as:

$$\text{Equilibrium Swelling Ratio} = \frac{W_e - W_d}{W_d}$$

, where W_e is weight of sample in equilibrium with water and W_d the dried sample.

Compression tests of gels at their swollen state were performed using universal testing machine (Tinius Olsen 1000).

Results and discussion

Particle size. Figure 1 shows the variation of dispersion size with NIPAAm content measured at two different temperatures, that is above and below the LCST. As the NIPAAm content increases, particle size increases at below the LCST. This indicates that NIPAAm monomers diffuse into the PU dispersion effectively. Moreover, particle size at 25°C is much bigger than that 50°C

regardless of the NIPAAm composition although the difference is increased with increasing NIPAAm content.

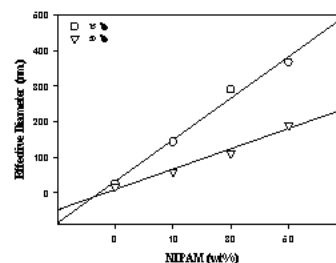


Figure 1. Particle Size of IPNs Dispersion.

Swelling properties. The temperature dependent equilibrium swelling of the dispersion cast films having various PU/NIPAAm compositions are given in Figure 2. Below the LCST, equilibrium swelling significantly increases with increasing NIPAAm content leading to a maximum increase of about three times for NIPAAm50 as compared with homopolymer PU. Above LCST, equilibrium swelling is lower than the one which is constant with temperature and composition except for PU. This result showed that the swelling ability of hydrogels increased and phase transition becomes faster with increasing NIPAAm content.

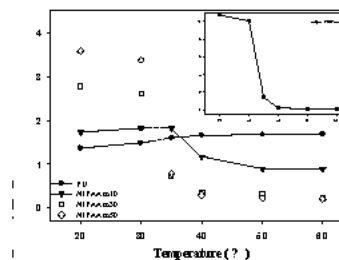


Figure 2. Equilibrium Swelling Ratio of IPNs Cast Films.

Compression properties. Compression properties such as modulus, strength and strain at failure for the PNIPAAm and PU-PNIPAAm IPNs are given in Figure 3. As the content of PU in IPN increase, the modulus monotonically increase and the strain at break monotonically decrease.

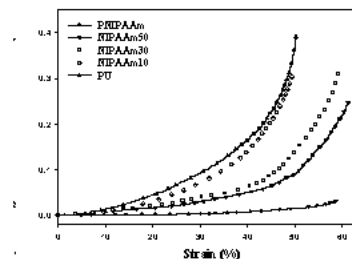


Figure 3. Compression Properties of PU/PNIPAAm IPNs.

Conclusions

The difference of particle size between above and below the LCST indicates much higher thermosensitivity of PU-PNIPAAm hydrogels. Equilibrium swelling at room temperature increased dramatically with NIPAAm and it was over about three times with 50wt% NIPAAm. Mechanical properties were increased with increasing PU content. These results showed that IPN-based PNIPAAm hydrogels from PU and PNIPAAm networks improve mechanical properties without weakening the thermal sensitivity of the hydrogels.

References

- [1] S. J. Hirotsu, *Chem. Phys.* **1988**, *88*, 427.
- [2] L. C. Dong and A. S. Hoffman, *J. Controll. Release* **1990**, *13*, 21.
- [3] S. H. Baek and B. K. Kim, *Colloid and Surface A* **2003**, *220*, 191.